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Injection of Hazardous Wastes into Deep Wells State-of-the-Art Report

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State-of-the-Art Report

INJECTION OF HAZARDOUS WASTES INTO DEEP WELLS

by

Arden Strycker and A. Gene Collins

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16. ABSTRACT

About 11 percent of all hazardous wastes are presently disposed of by injection wells into deep subsurface environments. There are approximately 250 of these Class I wells in the United States and to date their record of performance has been good.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by 1988 the U.S. Environmental Protection Agency (EPA) must show that the disposal of specified hazardous wastes is safe to the environment and human health, or deep-well injection practices must be discontinued. As a result, knowing the long-term fate of these wastes in the injection zone becomes important. The literature survey conducted in this work shows that some information is available on nearly all of the potential chemical and biological transformation processes of hazardous wastes. This survey indicates that many factors affect the ultimate fate of injected wastes and that additional research is needed in all areas of abiotic and biotic waste interactions before definitive explanations can be given on their long-term fate.

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FOREWORD

The U.S. Environmental Protection Agency was established to coordindate administration of the major Federal programs designed to protect the quality of our environment.

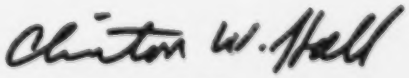
An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's land and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities.

As one of the facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment including zones for deep-well injection of hazardous wastes; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil, deep well injection zones and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by 1988 the Environmental Protection Agency (EPA) show that the disposal of specific wastes is safe to human health and the environment, or the practice of deep-well injection of hazardous wastes must be discontinued.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective and provide adequate environmental protection for the American public.



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ABSTRACT

About 11 percent of all hazardous wastes are disposed of by injection wells into deep subsurface environments. Some 250 of these Class I wells are in the United States, and their record of performance is good.

Provisions of the Resource Conservation and Recovery Act (RCRA) require that by 1988 the Environmental Protection Agency (EPA) show that the disposal of specified wastes is safe to human health and the environment, or the practice of deep-well injection of hazardous wastes must be discontinued. As a result, knowing the long-term fate of these wastes in the injection zone becomes important.

A survey of the literature performed in this work shows that some information is available on nearly all of the potential chemical and biological tranformation processes of hazardous wastes. This survey also indicates that additional research is needed in all areas of abiotic and biotic waste interactions before definitive explanations can be given on their long-term fate.

Usually, the first experimental test conducted is the fluid-fluid compatibility test of the waste with the formation fluids. However, research results show that this simple test is not always adequate for determining the interaction of injected wastes with the subsurface environment.

Many factors affect the ultimate fate of injected wastes. These factors include pH-Eh of the waste and reservoir fluids, brine concentration of the waste fluids, clay type and amount in the reservoir, presence or absence of iron oxides, presence or absence of organic complexing agents, molecular characteristics of organic materials, and other factors that determine if

the environment is anaerobic or aerobic. All of these factors are interrelated, and any mixing of different types of hazardous wastes in the reservoir further complicates the situation, making it difficult to predict exactly what occurs after the injection of wastes and their ultimate fate. Relevant research conducted to date concerning this problem has been limited and is not sufficient to address adequately the problem of predicting the ultimate fate of injected wastes.

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TABLE OF CONTENTS

	Page
Foreword	iii
Abstract	iv
Illustrations and Tables	vii
Acknowledgements	viii
Introduction	1
Processes Involving Non-Organic Hazardous Wastes	7
Compatibility of Injection Fluids with Reservoir Fluids	8
Effects of Metal Complexes on Their Mobility	13
Sorption Processes of Hazardous Wastes	16
Known Properties of Listed Metals	21
Arsenic	21
Cadmium	22
Chromium (VI)	22
Lead	24
Mercury	24
Nickel	24
Selenium	27
Thorium	27
Mathematical Models Used for Prediction of Fate	27
Processes Involving Organic Hazardous Wastes	29
Thermal Degradation	31
Adsorption Processes	32
Oxidation of Organic Hazardous Wastes	36
Hydrolysis of Organic Hazardous Wastes	36
Microbiological Degradation	38
Field Case Studies	42
Belle Glade, Florida	42
Wilmington, North Carolina	43
Pensacola, Florida (American Cyanamid)	45
Pensacola, Florida (Monsanto)	46
Conclusions	46
Recommendations	48
Phase II	48
Phase III	48
References	49

ILLUSTRATIONS

page

1. Distribution of molecular and ionic species of divalent cadmium at different pH values 23
2. Distribution of molecular and ionic species of divalent lead at different pH values 25
3. Distribution of molecular and ionic species of divalent mercury at different pH values 26

TABLE

1. Summary of results from survey conducted by EPA in 1983 4

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INTRODUCTION

The Environmental Protection Agency (EPA) estimates that Class I wells are used for the disposal of about 11 percent of all liquid hazardous wastes produced annually in this country. This corresponds to about 11.5 billion gallons of hazardous wastes that are injected into some 250 Class I wells.[1] Although these wells are located in sedimentary basins throughout this country, most of them are in the Great Lakes region and along the Gulf Coast.

The literature survey discussed in this report was initiated to determine what knowledge is available in the literature concerning ultimate fate of injected hazardous wastes. The discussion in this report is limited to the hazardous wastes listed in the Hazardous Wastes and Solids Amendments of 1984. This report also limits "ultimate fate" to a time reasonably determined by laboratory and field pilot techniques now available. Since knowledge of the interactions of complex waste mixtures is limited, much of the discussion relates to particular chemicals or chemical groups. Laboratory work and field observations are discussed. Because of the limited research conducted specifically for deep-well formations, literature reports that address the interaction of wastes by any method that has useful applications to deep-well formations were considered in the survey.

Increased concern of the fate of wastes after disposal has led to changes in chemical processes.[2] Indeed, under the Resource Conservation and Recovery Act (RCRA), the EPA is required to make some decision concerning the safety of underground injection of hazardous wastes by August 8, 1988. Although a study prepared for the Underground Injection Practices Council (UIPC) showed that to date only a few malfunctions have resulted in contamination of water supplies,[3] future practices will have to ensure that no additional contaminations will occur.

The Hazardous and Solid Waste Amendments (HSWA) of 1984, section 3004, subsections f and g, direct EPA to undergo a 45-month review of underground injection and to prohibit underground injection of certain wastes "if it may reasonably be determined that disposal may not be protective of human health and the environment for as long as the waste remains hazardous." The determination of what constitutes potential risk to human health or the environment is totally at the discretion of EPA. Additionally, EPA may apply any restrictions it considers necessary to ensure the safety of the disposal practices. If the safety of underground injection cannot be demonstrated by August 1988, disposal of hazardous wastes by this method will be prohibited by law.

The wastes referred to in the stated amendments include liquid wastes having any of the following properties and characteristics:

(a) Free cyanides ≥ 1,000 mg/l

(b) The following metals or compounds of metals: arsenic ≥ 500 mg/l, cadmium ≥ 100 mg/l, chromium (VI) ≥ 500 mg/l, lead ≥ 500 mg/l, mercury ≥ 20 mg/l, nickel ≥ 134 mg/l, selenium ≥ 100 mg/l, and thorium ≥ 130 mg/l

(c) A pH ≤ 2.0

(d) Polychlorinated biphenyls ≥ 50 ppm

(e) Halogenated organic compounds ≥ 1000 ppm

(f) Dioxin-containing hazardous wastes numbered as follows:

F020-production wastes of tri- and tetrachlorophenols and intermediates

F021-production wastes of pentachlorophenol and intermediates

F022-production wastes from tetra-, penta-, and hexachlorobenzenes

F023-production wastes from equipment used for the manufacture of tri- and tetrachlorophenols

F001-tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons used in degreasing

F002-methylene chloride, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, and fluorotrichloromethane

F003-xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, methyl isobutyl ketone, n-butyl alcohol, cyclohexanone, and methanol

F004-cresols, cresylic acid, and nitrobenzene

F005-toluene, methyl ethyl ketone, carbon disulfide, isobutanol, and pyridine

In 1983 the EPA surveyed 108 active hazardous waste wells for the type and amount of wastes injected.[1] The results of that survey (TABLE 1) show that most of the wastes categorized as hazardous contain either acid solutions or organic materials. The volume of water injected with these wastes was 6.2 billion gallons, or about 96 percent of the total volume injected; therefore, the amount of material considered hazardous is a relatively small portion of the total. The total percent of wastes injected (as listed in TABLE 1) is slightly greater than 100 percent due to some overlays in the categories; i.e., organic wastes and acid wastes.

A survey completed for the Chemical Manufactures' Association (CMA) investigated the wells and reservoirs used for disposing wastes such as those just listed.[4] From this study, a "typical" injection well might be described as having the following characteristics. The well is 3,925 ft deep with an injection zone greater than 200 ft thick. The injection zone is composed of sandstone/sand/silt, and the confining zone is composed of clay/shale silt.

TABLE 1. - Summary of results from EPA 1983 survey

Waste type	Percent of total gallons
Inorganic or organic solutions pH ≤ 2.0	20.3
Arsenic, barium, cadmium, chromium, lead, mercury, nickel	0.7
Organic	17.4
Selenium, cyanides	0.04
Other inorganics (non-hazardous)	52.0
Other (unknown)	9.9

The median wellhead pressure and injection flow are 285 psig and 150 gal/min.[4] Most of the facilities treat the wastes before injection. Common pretreatment practices include solids removal, equalization, and pH adjustment. About 96 percent of the total volume injected is water. Annular fluid and injection pressures are monitored continuously in most cases.

> Subsection g (HSWA) does contain a provision absent from subsection f, that specifies that a method of disposal may not be determined to be protective of human health and the environment unless upon application by an interested person, it has been demonstrated to the administrator, to a reasonable degree of certainty, that there will be no migration of hazardous constituents from the disposal unit or injection zone for as long as the wastes remain hazardous.[5]

Two general ways of satisfying this condition exist: 1) by showing that the wastes will never migrate out of the injection zone, or 2) by showing that the wastes become non-hazardous before they migrate to areas outside the injection zone.

Injection of hazardous wastes can be considered safe if the first condition is met. However, there are at least five ways a waste material may migrate and contaminate potable ground water:[6]

- Wastes may escape through the well bore into an underground source of drinking water (USDW) because of insufficient casing or failure of the injection well casing due to corrosion, excessive injection pressure, etc.
- Wastes may escape vertically outside of the well casing from the injection zone into a USDW aquifer.
- Wastes may escape vertically from the injection zone through confining beds that are inadequate because of high primary permeability, solution channels, joints, faults, or induced fractures.
- Wastes may escape vertically from the injection zone through nearby wells that are improperly cemented or plugged or that have insufficient or leaky casing.
- Wastes may contaminate USDW directly by lateral travel of the injected waste water from a region of saline water to a region of fresh water in the same aquifer.

The likelihood that any of these migration patterns will occur can be reduced greatly with proper design, construction, maintenance, good reservoir characterization, and monitoring of underground injection well practices.

Demonstrating the fate of injected wastes requires a knowledge of the behavior of each waste after it enters the subsurface environment. The interaction of a particular waste with other injected wastes, with reservoir fluids, and with reservoir solid materials, such as clays, silicates, and carbonates must be known. Unfortunately, hazardous wastes are complex mixtures of materials, and their combination with other mixed waste streams

increases the potential number of interactions factorially. Furthermore, since subsurface environments often take many years to reach chemical and biological equilibrium, predicting exactly what will happen *a priori* may be nearly impossible. For example, some toxic metals may adsorb onto clays as they are injected, making the migrating fluids immediately non-hazardous. This adsorption process does not guarantee that some waste injected into the reservoir in the future might lead to desorption of the same metals, thus rendering the fluids hazardous again.

The methodology for assessing fate generally is thought of as a description of all major chemical and biological pathways for movement or transformation of a chemical. This description includes that of concentration as a function of time for the original chemical and all subsequent products from transformation processes. Therefore, the chemical and biological interactions with the subsurface environment must be outlined to determine the fate of injected hazardous wastes and to decide when these wastes are no longer hazardous to satisfy the legislation using the second condition.

The first section following the introduction of this report discusses what is known about non-organic hazardous materials. Such major processes as neutralization, hydrolysis, ion exchange, precipitation, complexation, and adsorption are included in the discussion. As might be expected, organic materials not considered in the above list of hazardous wastes may strongly influence these processes and will be discussed as appropriate. Also, since the behavior of some non-organic materials is more easily quantified than organic materials, mathematical models were developed to help describe and predict their behavior. A short discussion of these models is also included.

The second section discusses what is known about hazardous organic materials. Such processes as thermal degradation, adsorption, oxidation,

reduction, hydrolysis, and microbial degradation are included in this discussion. Microbial degradation actually is a general term for many biological processes and will be discussed at some length.

Finally, the third section discusses several field case studies. This section is pertinent, since it deals with complex waste streams and integrates information presented in the previous two sections. Unfortunately, the literature available on case histories is limited.

PROCESSES INVOLVING NON-ORGANIC HAZARDOUS WASTES

One notable characteristic of most non-organic hazardous wastes, such as lead, cadmium, and chromium, is that they never go away. The only ways such materials can be rendered non-hazardous are by dilution, by isolation, and in some cases by changes in oxidation state. Therefore, waste treatment methods such as incineration are ineffective because the metal salts are not degraded by burning. Thus, deep-well injection is potentially useful if these hazardous materials remain isolated, or at least disperse to a residual concentration that is no longer harmful to human health or the environment.

The most likely reactions or transformations for non-organic hazardous wastes include precipitation, adsorption/desorption, ion exchange, hydrolysis, complexation, oxidation/reduction, acid/base reaction, and mineral dissolution. As mentioned in the introduction, the percent of total wastes injected that contain toxic metals is small ($\leq$ 1.0 percent). These include arsenic, barium, cadmium, chromium, lead, mercury, nickel, and selenium. Most of the non-organic wastes injected are classified as non-hazardous and contain various alkali metal salts, such as lithium, sodium, and potassium. The presence and concentration of these non-hazardous metals are important considerations when evaluating the fate of hazardous wastes. Their effects will

be discussed in more detail in subsequent subsections. The particular materials addressed as hazardous under this section include free metal and associated salts of arsenic, cadmium, chromium (VI), lead, mercury, nickel, selenium, thorium, inorganic salts of cyanide, and any solution with a pH lower than 2.0 derived from mineral acids.

The literature covered in this report indicates that the properties of non-organic materials in subsurface environments are more easily quantified, since the total possible reaction products available to any particular hazardous compound is finite and is limited by combinations of other materials found in the injection zone. Contrasting this definable situation is the study of organic materials, where the possible number of products are much more difficult to limit. However, the injection of non-organic wastes in subsurface environments appears to be more easily quantifiable, and the introduction of many different chemicals simultaneously or in succession rapidly increases the complexity.

Compatibility of Injection Fluids With Reservoir Fluids

Subsurface reservoir fluids have equilibrated with reservoir minerals and clays during geologic time. All of the minerals, rocks, hydrocarbons, gases, etc. are interrelated and contribute to the final stable solute/solvent matrix that exists in the reservoir. On the other hand, waste solutions considered for deep-well injection were generated in a different environment and have attained a thermodynamic equilibrium under different circumstances. Consequently, upon injection into the formation, adjustments must occur before a new solute/solution equilibrium is reached. Some injected wastes result in immediate precipitation of solids from solution and potentially may plug the formation from further injection. Other wastes may result in less immediate

problems but still may reduce the life of the injection well significantly. Thus, injection well operators usually conduct laboratory tests on injected hazardous wastes and native reservoir fluids to determine their compatibility.

Methods of testing for compatibility have been described.[7-10] Generally, the two fluids are simply mixed together and allowed to stand for some time. The formation of precipitate usually is an indicator of fluid-fluid incompatibility; however, some caution must be exercised.[7-10] The solutions should be kept at the temperatures and pressures of the reservoir; synthetic solutions are not as reliable as native reservoir fluids for accurate results; and sufficient time (hours to days) for incubation should be allowed. True thermodynamic equilibrium may not be achieved very quickly for some systems.

Reactions of injected and interstitial fluids that can produce precipitates in deep-well injection were discussed by Warner[11-12] and include:

- Precipitation of alkaline earth metals, such as calcium, barium, strontium and magnesium as insoluble carbonates, sulfates, orthophosphates, fluorides, and hydroxides
- Precipitation of other metals such as iron, aluminum, cadmium, zinc, manganese, and chromium as insoluble carbonates, bicarbonates, hydroxides, orthophosphates, and sulfides
- Precipitation of oxidation/reduction reaction products, such as hydrogen sulfide with chromium (VI).

Warner conducted some laboratory studies of these processes using a sand-pack model.[11] Some theoretical development accompanied the laboratory work as a means of evaluating the results. Warner's results showed that the amount of mixing between different fluids that occurred was dependent upon hydrodynamic dispersion processes. Once this dispersive property of the porous medium was characterized, the amount of chemical reaction could be accurately predicted.

Warner[11] also found that the type of precipitate that was produced also determined the degree of permeability reduction that resulted. For example, ferric hydroxide appreciably blocked the flow of fluids through a porous matrix, but barium sulfate and calcium sulfate did not. Ferric hydroxide is gelatinous in nature while barium sulfate and calcium sulfate are finely crystalline. The type of precipitate seemed to determine the effectiveness of blocking in the porous matrix.

One method of preventing injection wells from becoming plugged due to incompatible waters has been the injection of a buffer zone of nonreactive water. Warner showed in his laboratory model that a sufficiently sized buffer would effectively prevent a precipitation problem.[11]

Barnes[13] also points out that if the pH values of the two solutions are different, problems may result. For example, even though injected and interstitual fluids may be saturated with carbonate, having a different pH or calcium activities will make the solutions incompatible. The reason pH is so important is that ion concentrations are linear functions of the fluid proportions, but the equilibrium constants are not. Above pH 10, calcium, barium, strontium, magnesium, and iron will form gelatinous hydroxide precipitates. Lower pH solutions containing bicarbonates, will convert to carbonates if the pH is raised, and precipitates of iron, calcium, and magnesium carbonates may result. Many scale indices have been developed to predict potential precipitation problems.[14] However, these are not discussed here, other than to note that they exist.

An example of incompatible fluids was documented for the Arbuckle formation.[15] The reactions of chromates and phosphates in the waste stream with barium sulfate, hydrogen sulfide, and soluble iron formed precipitates that eventually plugged the well.[16]

Grubbs et al.[17] presented a good literature review of studies investigating incompatibility of injected fluids with reservoir fluids. Many of the studies showed that incompatible fluids can form precipitates that reduce the permeability of a porous matrix. Grubbs et al.[17] also studied the injection of liquid wastes with typical reservoir fluids and how incompatibility affected core plugs. Reduction of permeability and porosity was demonstrated and was shown to be greater at the input end of the cores. Temperature was found to be a more important variable than pressure when considering the conditions of a formation. Grubbs et al.[17] showed that while certain low pH solutions initially may leach some formation minerals, the solutions may also result in the precipitation of other minerals and actually reduce the permeability rather than increase it.

Another example of mixed fluid reactions studied by Ragone et al.[18] illustrated the complexity of predicting compatibilities. A particular recharge well in New York was studied using standard analyses of injected and native fluids from the injection well and observation wells. They observed a nearly 10-fold increase of ferrous ion concentration at the fluid interfaces over that of either the injected fluid or the native fluids. The most likely source of this increased iron concentration was thought to be from the pyrite in the Magothy aquifer. It was thought that the injected fluids changed the underground environment from a reducing to an oxidizing one. Under an oxidizing environment, pyrite becomes thermodynamically unstable and releases ferrous, sulfate, and hydronium ions as shown:

$$FeS_2 + 8H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^-$$

The produced acids are eventually neutralized, and the produced ferrous ions start to precipitate as ferric hydroxide in the presence of oxygen until a stable system is reached. This chemistry is further complicated by solution

pH, Eh, the presence of Fe^{3+}, partial O_2 pressure, presence of organics, etc. While it is not expected that all waste injection processes result in increased solubilities of iron, it does illustrate that the non-hazardous components, oxygen in this case, of a hazardous waste can have important influences on the overall chemistry and potential fate of hazardous wastes.

Hower et al.[19] discussed in some detail the potential interactions involved with incompatible injected fluids. Low concentrations of salts can lead to migration of clays. This has been demonstrated in the laboratory and in the field. High pH solutions tended to dissolve silica and release fines that would migrate and plug the pores, resulting in permeability damage to the formation. Additional formation damage may occur as the dissolved silica reprecipitates in another section of the reservoir.[20-21] Alternatively, low pH solutions may lead to silica gels or the dissolution of some clays and carbonate (either matrix or cements). All of these problems are not as evident in carbonate formations. However, later deposition of materials with changes in pH may also be a problem in carbonate formations.

The study of compatible and incompatible fluids with reservoir fluids was extensive in the past. Although brief, this discussion illustrates that what appears at first to be a simple test of compatibility--simply mix the fluids together in a test tube and allow it to sit--is inadequate to treat the many complexities that often occur. Examples of apparently incompatible fluids causing little trouble in the field and apparently compatible fluids plugging the injection wells were noted and further illustrate the inadequacy of this simple test.

Effects of Metal Complexes on Their Mobility

For non-organic hazardous wastes, toxicity is a function of solubility, and solubility determines the relative mobility of these materials in the reservoir. The more soluble the metal, the greater the rate of transport and the greater the magnitude of toxicity. Simple solution properties such as pH and Eh affect solubility, and these effects were discussed briefly with respect to certain materials.

However, the presence of other organic chemicals that may form complexes with these metals can also increase the solubility and, thus, are important when considering their fate.[22-24] For example, such chelating agents as nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA), and ethylenediaminetetraacetic acid (EDTA) are used in waste processing of radioactive wastes because they are effective in carrying these wastes away from the waste source.[22] Unfortunately, these same chelating agents may also enhance the mobility of the radioactive metals in the underground environment. The solubility of most metals are much higher when in the form of metal-organic complexes. To avoid the problem of waste migration, waste disposal includes a pretreatment to destroy the chelating agents prior to entering the formation.

Other organic chemicals can also have limited abilities to coordinate with metals. Such naturally occurring chemicals as aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols can all partially complex with metal compounds and increase their solubility.[22] Since, mobility is important in estimating potential health hazards, the presence of these compounds must be considered.

One of the most common aliphatic acids found in oilfield waters is acetic acid. A study covering 95 formation water samples in California and Texas

found that the presence or absence of acetate anions was dependent upon the zone from which the samples were taken.[25] Most of the acetate ions were found in zone 2 (temperature range of 80°-200° C). At temperatures greater than 200° C, very little was found. The authors claimed that thermal decarboxylation was probably the mechanism of acetate degradation.[26] Very few aliphatic acids were found in zone 1 (temperatures lower than 80° C) as well.[22] The authors explained the absence of acetate ions in this zone as an example of microbial degradation by methanogenic bacteria.[22] Dilution by mixing with other waters was also thought to contribute.

Although the degradation of organic materials under anaerobic conditions has not been extensively studied, some work has been done. Novak and Ramish[27] discussed anaerobic degradation as a multi-step process in which complex compounds are broken down by certain facultative bacteria, and the resulting short-chain acid anions are broken down by methanogenic bacteria. Other mechanisms have also been proposed, but will not be discussed further (see reference 22 and references therein).

A study of adsorption/desorption properties of uranium, cobalt, strontium, and cesium showed that chelating agents that enhance the solubility of these metals in water do not necessarily decrease adsorption.[23] These organic compounds are known to enhance the solubility of metals, but in the presence of clays the enhanced solubilities were not always predictable. Cobalt was found to be less strongly adsorbed when these materials were present. However, strontium and cesium were not affected, and uranium was more strongly adsorbed. The authors suggested that the uranium/acid complex may have a greater tendency to adsorb to the clay surface than the individual metal, because of additional electrostatic and molecular dipole attractive forces from the complex.

Other evidence supports the idea that the presence of chelating agents do not always have obvious results. Champlin[28] discussed the various energies associated with complexing agents, ion exchange processes, and adsorption processes. Some of the values showed that the energies associated with chelating agents were approximately of the same magnitude as those of cation-silicate interactions. Thus, slight differences in conditions may have major impact on the overall results.

Complexities are encountered when the concentrations of the metals are considered.[23] For example, when ferric ion is in low concentrations, natural organics such as humic acids form true solutions due to metal-organic complexes. However, at higher ferric ion concentrations, colloidal suspensions are formed from the same humic acids. Metal complexed compounds may have reduced intermolecular repulsion forces in the complexed molecule. As a result, the organic material would recoil and become less hydrated in the solution since all of the polar sites are taken up by the metal. Such a particle then would remain suspended or precipitate depending upon the particle size. Variations in pH will further complicate the chemistry since all of these reactions are affected by the solution pH.

Additional complexity is introduced when bacteria are considered. Not only can bacteria degrade the organic components of metal/organic complexed particles, but bacteria may also convert some non-complexing materials into complexing agents.[24] A conceivable situation might include the injection of a hazardous waste into a well containing certain non-hazardous materials that support such a bacteria. The production of bacterial wastes capable of enhancing the solubility of certain metals would increase the potential hazard by increasing the mobility of toxic metals. Alternatively, the same bacterial

wastes may increase the adsorption of the metals due to the enhanced adsorption properties observed for some metal/organic complexes.

Even though non-organic hazardous wastes are considered in this section, note that the presence or absence of certain organic chemicals is important in determining the fate of non-organic hazardous wastes. The identity and concentrations of naturally occurring organic compounds capable of forming coordination bonds with metals should be determined before injection. Also, the identity and quantity of organic compounds injected either simultaneously or in succession with metal wastes should be determined, even though the organic portion may not be considered as hazardous waste. Additionally, the presence of bacteria capable of generating complexing materials should not be ruled out. Each injection system should be considered in detail to determine the relative importance of metal-organic chemical interactions.

Sorption Processes of Hazardous Wastes

Although reactions between hazardous wastes and silica, dolomite, etc., are relatively straightforward and reactions between waste and reservoir fluids can often be easily characterized, the interactions between waste materials and formation clays have been difficult to characterize. Obvious interactions such as clay swelling and clay particle migration are possible with any injected fluid. In secondary and/or tertiary petroleum recovery operations, petroleum engineers usually avoid injecting alkaline solutions and sometimes all aqueous solutions when water-sensitive clays are present. Damage to the clays can result in drastically reduced permeabilities, and often specialized products that stabilize clays are used in treating fluids to prevent damage to reservoirs.

The adsorption of organic and non-organic materials varies, depending upon the amount and type of clay present in the formation because different clays have different surface areas and charge densities. Since clays possess an overall negative charge, cations such as moderately soluble metal wastes are attracted to these clays.[29] The more soluble ions previously attached to the clays may resolubilize when other less soluble ions replace them on the clay surface.[29] This process is termed ion exchange. Some of the metals associated with the clay may bond so tightly that they may be considered immobile or permanently adsorbed. Heavy metals are particularly susceptible to this behavior.

Clays can become saturated with a particular ion when all of the sites are filled and no further adsorption would result for that ion. Not only is this saturation level dependent upon the amount and type of clay present, it is also dependent upon whether iron and manganese oxides are present. Such oxides tend to provide good surface properties for adsorption.

Clays are typically composed of alternating layers of tetrahedral silicon oxide and octahedral aluminum oxide; however, occasionally the silicon or aluminum ions are replaced with other ions having lower oxidation states, which results in a net negative charge.[30-31] Since the degree of charge is highly dependent upon the conditions of the clay deposit, this exchange of ions is not uniform throughout the clay or between different clays, and explains why different clays behave differently.

Adsorption of water between these layers of clay crystals leads to swelling of the clay. Originally, the layers of clay crystals tend to stack over each other to bring the positive and negative charged faces close together and neutralize some of the negative charge of the material.[7] If a low salinity solution or a high pH solution contacts these layers, water molecules

start to adsorb and separate the layers from each other. These realigned crystal layers usually will not return to the original state, even if higher salinity solutions are again added to the clays.

Carl Veley[32] describes the adsorption process in more detail. The clay particle is pictured as being negatively charged as already explained. Exchangeable cations are attracted to this concentration of negative charge, but because of electrostatic repulsion these cations try to avoid each other. Veley describes the area near the negative charge of the clay as a tiny atmosphere that is most dense near the surface, becoming more diffuse at farther distances. If the solution is highly saline, there are many ions to counteract the repulsive forces between 'atmospheres' around the clay. Thus, the 'atmospheres' will be stable and ion exchange rates will be slow. However, if the surrounding solution has low salinity, the atmospheres will need to become more diffuse to avoid the repulsive forces of the cations. These less dense atmospheres will then lead to a loosening of the clay structure--swelling and migration.

Different cations also pack differently to form different density atmospheres around the clays. Veley[32] illustrated this point with a sandstone core containing some clay. The core was first treated with 3 percent calcium chloride followed by deionized water. The deionized water led to a less dense cation structure, but the calcium ion was attracted strongly enough to prevent migration of fines. When the same core was treated with 3 percent sodium chloride (replaced calcium with sodium) followed by deionized water, the core plugged. The sodium did not bind as strongly to the clay, and when the core was treated with deionized water the 'sodium atmospheres' were not densely packed enough to maintain the clay structure.

Polyvalent metal ions bind even more strongly to the clays. The metal first hydrates to some generalized form as described below.

$$M(H_2O)_N^{Z+} X^{Z-}$$

After hydration, the metal begins to hydrolyze and form multiple associations with other metals, such as the generalized form described below.

$$[M_x(OH)_y(H_2O)_N]^{L+}$$

When these complex polynuclear ions associate with the clay particles, a very tight structure around the clay crystal is formed. Months or years may be required before true equilibrium is reached between all of these different metal associations.

A core test similar to the one previously described was conducted. First, the core was treated with one of these hydrolyzable metals. The core was then treated with three subsequent solutions in order: deionized water, 3 percent sodium chloride solution, and deionized water. In contrast to the previous experiment, little reduction in permeability was observed. Unlike the calcium ions, the polynuclear ions were bound very tightly to the clay and were not replaced by sodium when treated with the sodium chloride solution.

This strong adsorption behavior may be very useful for certain hazardous wastes. If these wastes underwent such strong adsorption to the clays, the clays would be protected from swelling and fines migration and the well would be protected from being plugged prematurely. Also, the wastes would be isolated from man's environment, since the wastes are rendered immobile by permanent adsorption in the injection zone.

However, another situation needs to be considered. Suppose adsorbed metal ions were attached to very small particles of clays. If the clay particles remain unattached to the silica matrix of the reservoir, the metal would still be capable of migrating as a metal-clay particle. Champlin[28] did an extensive study of the forces affecting adsorption and ion exchange processes with clay particles and metal ions and found that this mechanism of mobility can be very important.

Champlin divided the particle forces into two types: physical forces and chemical forces. Physical forces include the interactions between the suspended particles, the interaction between the suspended particles and the grains of the sand bed, and the interaction between the suspended particles and the earth itself in the form of gravitational effects. Accordingly, the particles may aggregate, adsorb onto rock surfaces, or drop out of the suspension, depending upon which of these forces predominate. Alternatively, a pseudo-equilibrium may be attained if the energies of these forces are not great enough to overcome the mean thermal energy of the system.

To study these physical forces, Champlin conducted flow experiments through cores and measured the ion and particle concentrations throughout.[28] He found that when the salinity of the effluent was low, both the ions and particles were strongly retained by the sand in the core. When the salinity of the water was high, both the ions and suspended particles passed through the core and were not retained by the sand. Most importantly, isotopic labeling led him to further postulate that when the ions and particles passed through the core, the ions were still attached to the migrating particles. Thus, a mechanism was proposed where salinity affected the attractive forces between the suspended particles and the sand grains. The physical and

chemical forces of the metal ions were sufficiently strong to remain attached to the clay particles.

Certainly, clays provide a surface capable of attracting certain non-organic hazardous wastes. The adsorption of these wastes onto the clays in the injection zone is desirable, since the mobile fluids would be rendered less hazardous, and the clays may be protected from additional swelling and migration. Of course, the adsorption of materials is not desirable when such processes result in the plugging of the well. Predicting how much waste will be adsorbed, how long the waste will remain immobile, and under what circumstances the waste will be desorbed is difficult.

Known Properties of Listed Metals

Arsenic

In general, arsenic cations are more mobile under anaerobic conditions than aerobic conditions. Arsenic cations are more mobile than selenium, cadmium, and lead under anaerobic conditions when the pH is neutral to alkaline.[33] Some microorganisms are capable of converting $As(OH)_3$ to $As(CH_3)_3$ under anaerobic conditions.[33]

Certain forms of arsenic are known to react with limestone to produce carbon dioxide. These include As_2O_3, $(CH_3)_2AsO_2H$, and $Mg_3(AsO_3)_2$. Certain forms are known to react with granite to hydrolyze the potash feldspar minerals. These include As_2O_3, $Ca_3(AsO_4)_2$, $(CH_3)_2AsO_2H$, $CaHAsO_3$, $KAsO_2$, Na_2HAsO_4, and Na_3AsO_3. Certain forms of arsenic are also known to adsorb on shales with varying amounts of clay. These include As_2O_3, $Ca_3(AsO_4)_2$, $CaHAsO_3$, $PbHAsO_4$, $Pb(AsO_2)_2$, $Mg_3(AsO_3)_2$, $MnHAsO_4$, $KAsO_2$, Na_2HAsO_4, Na_3AsO_3, and $Zn(AsO_2)_2$. All of this information can be found in reference 36.

Cadmium

The solubility of cadmium is less than that of some other metals, but more than that of lead. Figure 1 illustrates relative solubilities as a function of pH and cadmium species.[33] Figure 1 shows that at higher pH values, mixtures of hydroxides in various concentrations will exist.[33-36]

The presence of oxides and hydrous oxides of iron have been observed to increase adsorption properties of cadmium.[37] A threshold of the amount adsorbed exists and is dependent upon solution Eh and pH.

Some forms of cadmium are known to react with limestone to produce carbon dioxide. These include $CdCl_2$, CdF_2, and $CdSO_4$. Certain forms are known to adsorb to certain shales containing varying amounts of clays. These include $CdCl_2$, CdF_2, and $CdSO_4$.[36]

In the presence of hydrogen sulfide, cadmium will precipitate as cadmium sulfide.

Chromium (VI)

A striking characteristic of chromium is its mobility. In neutral to alkaline conditions, chromium is more mobile than most of the other metals listed. Under oxidizing conditions (aerobic) in soils, chromium will form insoluble precipitates with resident biological materials.[33]

The oxidation state of the chromium is also important. For example, chromium (III) can adsorb strongly in acid solutions and precipitate at pH values above 6 (as hydroxide, carbonate, or sulfide). Chromium (VI) does neither of these things.[33]

As with cadmium, chromium (VI) can adsorb onto oxides and hydrous oxides of iron.[37]

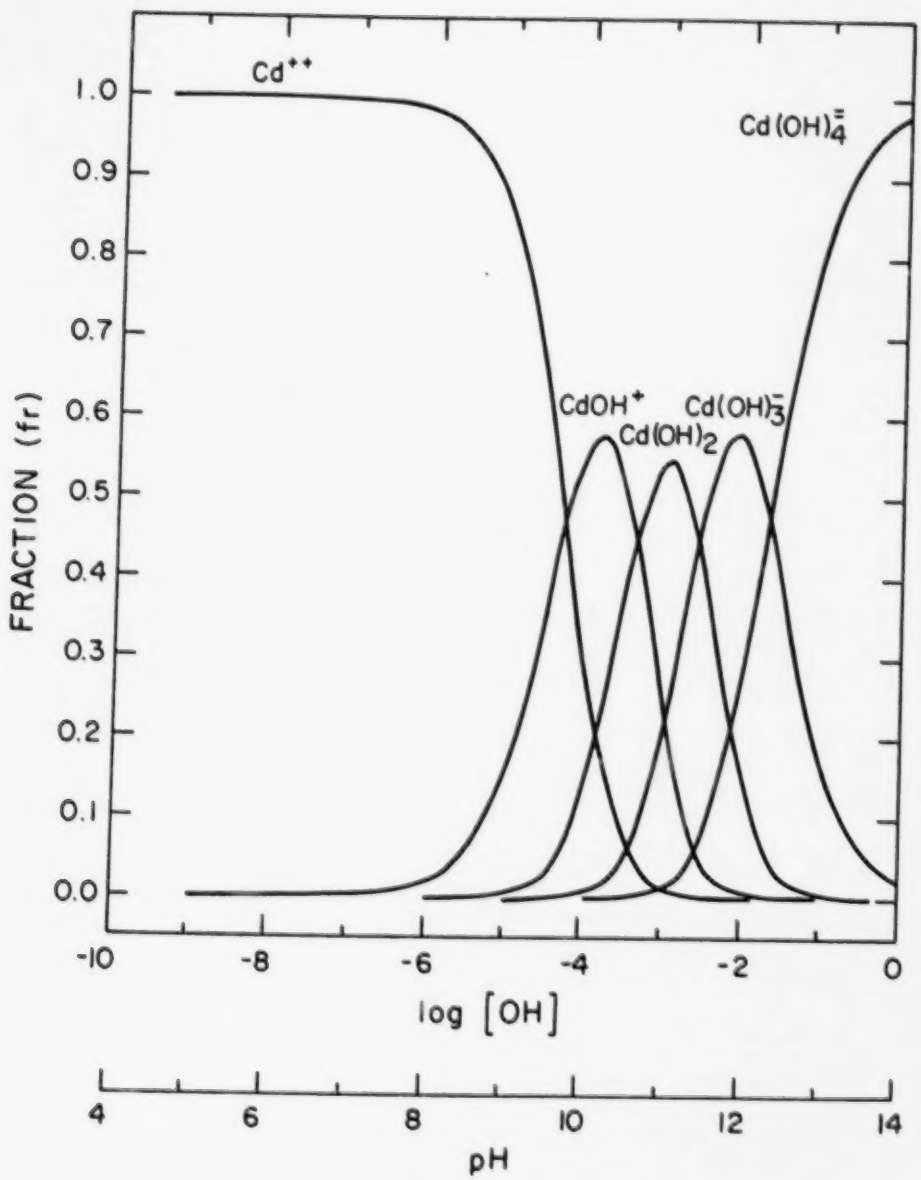

FIGURE 1. Distribution of molecular and ionic species of divalent cadmium at different pH values[33].

Lead

Lead is not very mobile under most subsurface conditions. That suggests that solubilities are lower and tendencies toward adsorption are higher than for most of the other metals listed.[33] Typical precipitates of lead include $Pb(OH)_2$, $PbCO_3$, and $Pb_5(PO_4)_3OH$.[34-35] Figure 2 illustrates the effects of pH and lead ion species on the solubilities of lead in solution.[33] The presence of sodium chloride does increase the solubility somewhat.[36]

Mercury

The major problem with mercury in soil environments is the volatility of mono and methyl mercury compounds.[36] However, the hazards presented by volatility in deep-well injection systems are unknown. Figure 3 shows the affect of pH and ionic form on the solubility of mercury.[33] As with some of the other metals, mercury compounds strongly adsorb to iron oxides if present.

One of the unique properties of mercury compounds is the ability of a bacteria, Methanobacterium omelianskii, to convert inorganic mercury compounds to methyl mercury.[33] Methyl mercury is considered more toxic and more volatile than the inorganic counterparts. Whether or not this occurs in injection zones for deep-well systems is unknown.

Nickel

As with some of the other metals, nickel compounds adsorb strongly in the presence of iron and manganese oxides. Nickel is not very soluble in the presence of carbonates, hydroxides, or sulfides.[33] Salts of nickel that are soluble include nickel acetate, chloride, nitrate, and sulfate.[36] Nickel oxides also may be solubilized in strong acid; however, as strong acids are neutralized in the reservoir, these oxides may then precipitate out.

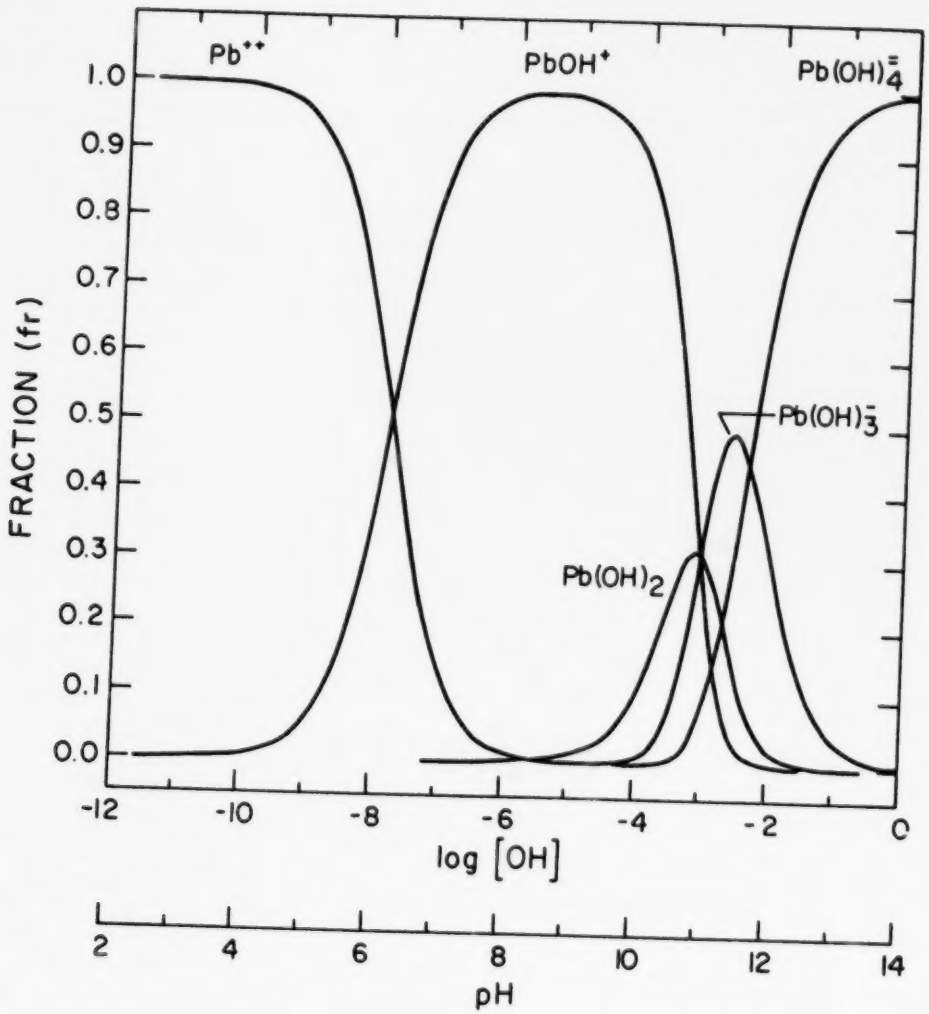

FIGURE 2. Distribution of molecular and ionic species of divalent lead at different pH values[33].

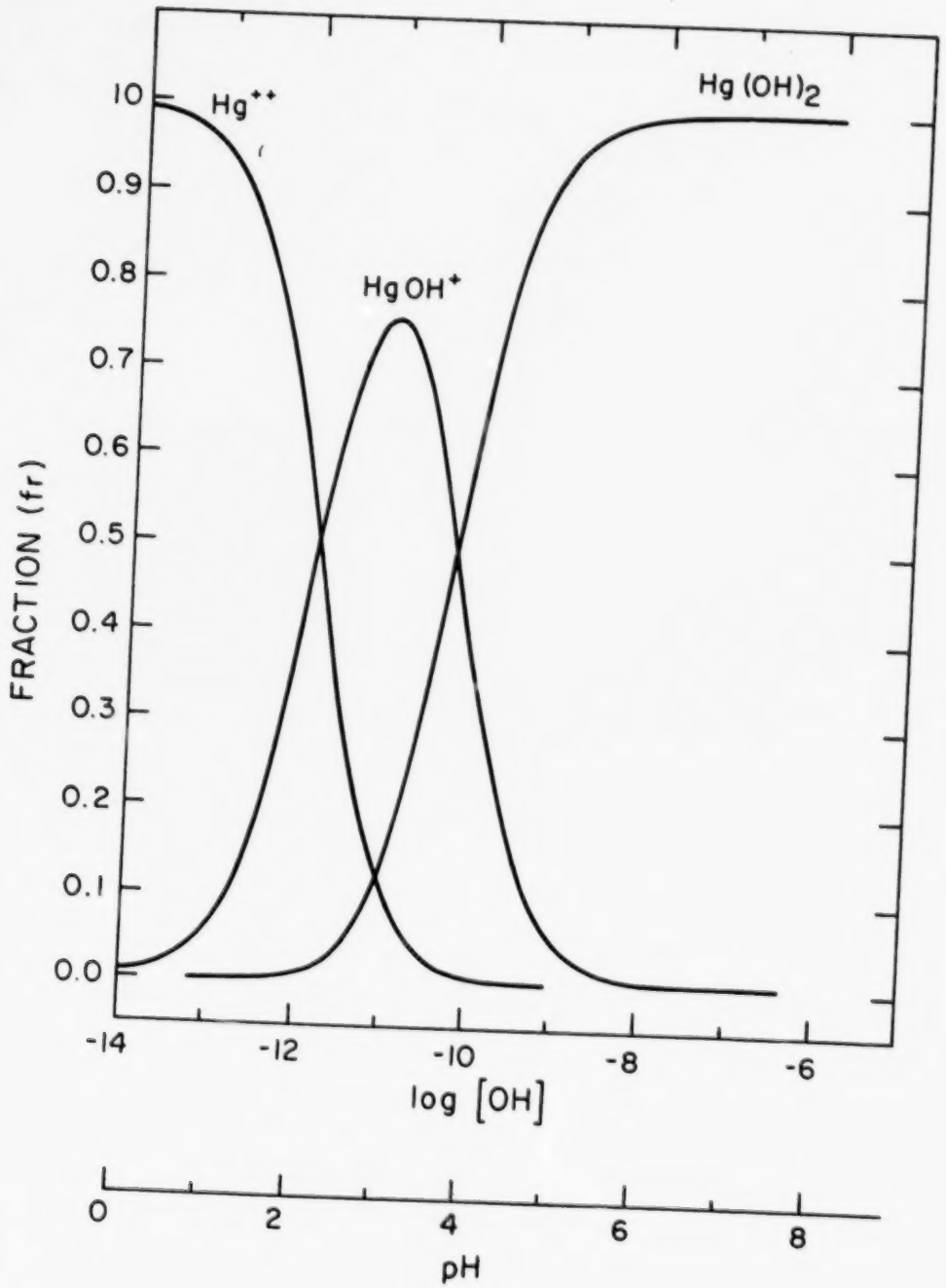

FIGURE 3. Distribution of molecular and ionic species of divalent mercury at different pH values[33].

Nickel carbonyl is also very toxic and when concentrated, potentially explosive. Nickel carbonyl is not decomposed in dilute acid or basic solutions but will produce cabon monoxide and nickel metal when heated.[37]

Selenium

As with some of the other metals, some selenium compounds adsorb more strongly in the pressure of iron oxides.[38] Selenium dioxide is readily soluble in water and forms selenous acid in aqueous solutions.[39] Common forms of selenium include H_2Se, Se_2Cl_2, $SeCl_4$, SeO_2, SeO_3, H_2SeO_3, H_2SeO_4, $CaSeO_3$, $BaSeO_3$, Se_2O_5 and K_2SSeO_3. Many of these compounds can be reduced to produce selenium metal when exposed to organic matters in the subsurface environment.[40]

Thorium

Thorium salts are not very soluble in neutral pH natural waters. Those salts of thorium that are soluble are those of sulfates, chlorides, and some sulfides. However, as the solution becomes basic, these salts are converted to the hydroxide, $Th(OH)_4$, and precipitate out.[40] It is interesting that the effect of temperature on the solubility of thorium sulfides depends upon the hydrate being tested. For example, $ThS_2 \cdot 9H_2O$ increases in solubility with increasing temperatures, while $ThS_2 \cdot 4H_2O$ decreases in solubility.[40] The more common hydrate is $ThS_2 \cdot 8H_2O$.

Other known salts of thorium include $BaThO_3$, $(NH_4)_2Th(NO_3)_6$, $Th_3(PO_4)_4$, $Th(HPO_4)_2$, ThP_2O_7, ThS_2, $Th(SO_4)_2$, ThO, and ThO_2.

MATHEMATICAL MODELS USED FOR PREDICTION OF FATE

Several research projects have concentrated on the modeling of some of the processes just discussed. Schechter et al.[41] present a good review of some models in the areas of aqueous geochemistry and solution chemistry. If a

particular situation can be defined as containing specified components, equilibrium constants can be approximated and the overall results predicted. Certain thermodynamic parameters are known for many of the materials of interest and provide a reasonable base from which to start. The report by Schechter et al.[41] provides a more detailed discussion of these modeling systems. Some of the more popular models discussed include: WATEQF, SOLMNEQ, PHREQE, EQ3/EQ6, PATHI, MINEQL, MINEQLI-STANFORD, PHASEQL/FLOW, and REDEQL.[42]

Roberts et al.[43] present a good review on some mathematical models for simulating the transport of wastes in an underground aquifer. These models attempt to predict the advection, dispersion, and sorption behavior of non-degradable organic solutes. Actual field cases were examined and compared with theoretical and laboratory results. The study showed that adsorption processes could be predicted with some accuracy; however, they found it necessary to measure the advective and dispersive properties in the underground environment. Theoretical and laboratory studies were not sufficient to predict the behavior in the field accurately.

Mills et al.[44] present a summary of five models that can be used to predict contamination in ground water. These models calculate contaminant concentrations as a function of time for a given set of conditions. Two models are radial one-dimensional, one model is cartesian one-dimensional, and two models are cartesian two-dimensional. Such parameters as boundary conditions, aquifer dimensions, dispersivity coefficients, porosity, initial contaminant concentrations, and retardation factors are needed as input to these models.

Kayser and Collins[45] present a summary of some of the models relevant to ground water contamination from enhanced oil recovery (EOR) or other fluids. The four types of models discussed include the groundwater flow model, solute

transport model, heat transport model, and deformation model. Each of these model types is based on different dependent variables and is particularly useful for answering different types of questions.

The intent of this section was primarily to indicate that if certain processes are well defined, they can be usefully modeled. Such models allow researchers to predict the fate of certain chemicals for a given situation. As shown already, many non-organic hazardous waste materials contain compounds that have been extensively studied in the laboratory. The existence of this knowledge is the reason development of mathematical models has been possible; however, as previously stated, the underground environment contains additional variables that have not been studied extensively. Thus, the degree of uncertainty in fate prediction by these methods is still large, and correct answers still must be obtained from tracer and pilot tests in the field.

PROCESSES INVOLVING ORGANIC HAZARDOUS WASTES

Unlike that of non-organic hazardous materials, the organic hazardous wastes can be made non-hazardous by molecular transformations of the compounds. Such processes as ion exchange, oxidation, reduction, hydrolysis, cyclization, and biological transformations are all possible means of rendering the wastes non-hazardous. Alternatively, these same processes can lead to increased toxicity for certain wastes. Because the number of potential products is almost infinite, assessing the "ultimate fate" of these wastes is even more difficult than for the non-organic hazardous wastes. For example, the conclusions of one study[46] for the injection of organic wastes at Wilmington, NC, suggested that all of the following chemical and biological processes occurred:

- dissolution of carbonate minerals by organic acids and production of carbon dioxide
- dissolution and complexation of iron derived from sesquioxide coatings on granular materials in the aquifer by organic acids
- reprecipitation of complexed dissolved iron during waste neutralization
- coprecipitation of phthalic acid complexed with iron during iron precipitation
- methane gas production from microbial degradation
- microbial reduction of sulfates to sulfides
- reduction of ferric ion to ferrous ion from Eh and pH changes due to microbial waste degradation
- retention of organic waste acids by adsorption and ion exchange onto the injection-zone mineral constituents
- formation of ferric hydroxide, ferric carbonate, terephthalic acid as precipitates, and carbon dioxide which led to the plugging of the wells

The report by Callahan et al.[47] gives a good summary of the expected fate for 129 non-organic and organic hazardous waste compounds. Although this report addresses the aquatic environment and not deep-well injection zones, the information provides a good beginning.

Whether the environment is aerobic or anaerobic determines what biodegradation processes will predominate. The types of organisms that dominate under aerobic conditions do not dominate under anaerobic conditions. Since some wastes are degraded more easily by aerobes and others are degraded more easily by anaerobes, the prevailing conditions will determine which wastes will be degraded. Furthermore, waste solutions

introduced into the subsurface environment may change a predominately aerobic environment to an anaerobic environment. Jackson et al.[48] summarize the expected probability of transformation for some organic compounds under different conditions. For example, chlorobenzenes are likely to degrade under aerobic conditions but not under anaerobic conditions. Conversely, carbon tetrachloride is not likely to degrade under aerobic conditions but is likely to degrade under methanogenic and denitrification anaerobic conditions.

A brief discussion of the various processes of degradation available to organic wastes will be presented in this section. The details of the discussions are shorter than the corresponding discussions for non-organic materials because (1) hardly any definitive work has been done and (2) the number of possible interactions is much greater than that of non-organic materials, making definitive fate predictions more difficult to determine.

Thermal Degradation

Such processes as oxidation, reduction, hydrolysis, adsorption, and microbiological degradation are common methods of transformation for organic hazardous wastes. Other transformation processes that are initiated thermally are possible and should be considered here as thermal degradation. These processes might include pyrolysis, condensation reactions, cyclization, intra-molecular rearrangements, etc. However, most of these processes are dependent upon either very high temperatures or the presence of other chemicals.

The reservoir temperatures and pressures commonly existing in the injection zones of the hazardous waste injection wells are normally too low for initiating high-temperature reactions. However, if the right chemicals (not necessarily the hazardous chemicals listed) contact some of the hazardous

wastes, these other processes listed in the first paragraph are possible. For example, phenols can react with formaldehyde to form phenolic resins. The number and type of these chemical interactions are limitless. Because the actual chemical reactions are dependent upon the presence of other specific chemicals, each reservoir and waste composition should be evaluated individually to determine what reactions and reaction products are likely.

Adsorption Processes

Adsorption is a major mechanism of fluid-solid interactions that affect the mobility of organic wastes. Adsorption has been found to be dependent upon the particular clays present. That is, montmorillonite and vermiculite have very high adsorption capacities, while kaolinite has a very low adsorption capacity. Illite and chlorite are intermediate in their ability to adsorb.[49] These properties have been attributed to the available surface area for the respective clays.

Many factors influence the degree of adsorption of various chemicals. Some of these factors include chemical shape and configuration, acidity, water solubility, charge distribution, polarity, molecular size, and polarizability.[49] Most organic compounds that adsorb on clay materials have contributions from all of these properties. Thus, predicting the degree of adsorption according to relative acidity may lead to incorrect predictions if resonance stabilization is not considered.[49] Molecular shape may increase or decrease the adsorption energies of any particular compound, even though the other chemical properties may be very similar. All of these listed properties have been demonstrated to be important and are found to be interdependent.

Another factor that influences adsorption is temperature. Since adsorption processes are generally exothermic and desorption processes are

generally endothermic, an increase in temperature would normally reduce adsorption processes. However, a number of exceptions have been found.[42] The pesticide EPTC is an example.

The mechanism of adsorption may occur by one of several different mechanisms for organic chemicals. These mechanisms include ion exchange, protonation at the silicate surface, protonation in the solution phase with subsequent adsorption by ion exchange, and protonation by reaction with the disassociated protons from residual water present on the surface or in coordination with the exchangeable cation.[49] The most easily adsorbed organic compound by ion exchange is that of the cation. The process is much the same as that which occurs for inorganic materials and is well documented.[49] Other methods of adsorption include chemical adsorption via Van der Waals forces, hydrogen bonding, and coordination with metals.

Several specific studies were conducted with pentachlorophenol.[50-51] These studies explained how pentachlorophenol was adsorbed via a combination of ion exchange and Van der Waals forces. The study also was careful to show the pH dependencies of the process. For example, in acidic solutions pentachlorophenol was found to decrease in concentration by precipitation, but at pH values greater than 5 the drop of concentration in the presence of clay was due to adsorption, not precipitation.

The affect of temperature on adsorption of pentachlorophenol was contrary to expectations. For four different clay samples, adsorption of pentachlorophenol was greater at higher temperatures (33° C) than at lower temperatures. Admittedly the temperatures were not indicative of deep-well environments, and no one has determined whether this trend would continue with even higher temperatures.[50]

As expected, an increase in concentration of other salts in the solution corresponds to a decrease in the amount of adsorption of pentachlorophenol.[50] This observation supports an ion exchange mechanism for the adsorption process and compares similarly to the results obtained for non-organic materials.

Mortland[52] also discusses some of the mechanisms by which organic chemicals are adsorbed. These include the replacement of metals with cationic molecules, replacement of metals by neutral molecules that are protonated to become cationic, ion exchange with polyvalent metals attached to the clay, coordination with metal cations, and by hydrogen bonding. Many of these mechanisms have been studied and demonstrated using such techniques as adsorption isotherms, calorimetry, X-ray diffraction, UV-visible spectroscopy, electron spin resonance spectroscopy, and infrared spectroscopy.

Once adsorbed, other processes may take place that lead to degradation of the adsorbed materials. For example, microorganisms may concentrate at the solid surface and metabolize the organic wastes. The organic compounds may undergo other chemical reactions if the clays or minerals attached to the clays can catalytically initiate other such reactions. McAuliffe and Coleman[53] have demonstrated this process to occur with hydrolysis of esters. Other examples also are discussed by Mortland.[52]

The adsorption of trichloroethylene and pentachlorophenol on several Missouri soils was discussed by O'Conner et al.[54] Trichloroethylene was not found to adsorb as readily as pentachlorophenol. Both were found to adsorb less as the pH was increased.

Rogers and McFarlane[55] studied the adsorption of carbon tetrachloride, ethylene dibromide, and chloroform on montmorillonite clay. The adsorption of the materials tested depended upon the conditions and materials tested. For

example, neither carbon tetrachloride or chloroform adsorbed onto calcium saturated clay, but chloroform showed 17 percent sorption on aluminum saturated clay. The mechanism for this difference was not understood.

Sorption studies of some chlorinated benzenes were discussed by Scharzenbach and Giger.[56] They found that for typical concentrations in the natural environment, a linear sorption isotherm could be used. As organic carbon increased, adsorption also increased.

Haque et al.[57] briefly discussed adsorption processes in soil. Adsorption processes are dependent upon factors such as structural characteristics of the molecule, organic content of the soil, pH of the medium, particle size, ion exchange capacity, and temperature.

The Freundlich isotherm often is used to evaluate adsorption of chemical compounds:

$$x/m = KC^n$$

x--amount of chemical adsorbed

m--mass of soil

C--equilibrium concentration of the chemical

K--constant describing extent of adsorption

n--constant describing the nature of adsorption

Generally, as the solubility of the adsorbate decreases, adsorption increases, and as organic content of soil increases, adsorption increases. However, ionic compounds or compounds capable of becoming ionic do not necessarily follow the Freundlich isotherm concept. Of course, these studies refer to soil. The usefulness of the Freundlich isotherm concept for adsorption in deep-well injection zones was not discussed.

Oxidation of Organic Hazardous Wastes

Another process by which certain hazardous organic wastes can be transformed into other compounds is by oxidation reactions. Such compounds as phenols, aromatic amines, olefins, dienes, alkyl sulfides, and eneamines are particularly susceptible.[58] The exact species of different oxygen radicals present in aqueous and soil environments that initiate the oxidation process may include such oxy-radicals as HO•, RO•, and $^1O_2$, depending upon the environmental conditions. The potential importance of this process at typical injection well conditions to hazardous waste injection has not been evaluated. However, if certain hazardous wastes containing chromium (VI) are co-injected either simultaneously or sequentially with organic wastes, the oxidation process most certainly will be important. Chromium (VI) can be an excellent oxidizing agent.

Hydrolysis of Organic Hazardous Wastes

Hydrolysis is the chemical process by which some functional group attached to a molecule is replaced by an -OH functional group originating from a water molecule. Hydrolysis can be catalyzed by either an acid or a base, as defined in chemistry for Lewis acids and bases.

Mabey and Mill[59] provide a good review of hydrolysis processes of organic materials in the environment. Factors such as pH, temperature, and the presence of other ions are known to affect the rate of hydrolysis. Depending upon whether the pH is high or low, different mechanisms may apply. At low pH, the hydronium ion (H_3O^+) predominates in hydrolysis, while at high pH, the hydroxide ion (OH^-) predominates. Although the effect of temperature is known, the magnitude of the influence that temperature has on different

compounds is not always known. The presence of certain alkaline earth and heavy metal ions may catalyze hydrolysis for a variety of esters.

The effect of pH can be illustrated with aliphatic and allylic halides. Hydrolysis may occur for these halides at neutral or basic conditions to give alcohols but are not likely to undergo the same process at acidic conditions. The type of halide being considered also affects the rate of hydrolysis. The rate constant for phenyl dichloromethane is about five orders of magnitude greater than that for dichloromethane. Chlorobenzene is virtually resistant under normal circumstances to hydrolysis.

Most of the hazardous wastes studied that can potentially undergo hydrolysis reactions are halogenated hydrocarbons, such as carbon tetrachloride, ethylene dibromide, and chloroform. Most of the results to date are derived from conditions most likely to occur near the surface of the earth. For example, ethylene dibromide has a half-life of 5 to 10 days, whereas carbon tetrachloride is much more resistant and has a half-life of 700 to 7000 years and that of chloroform is somewhere between these two ranges of values. Subsurface environments may lead to shorter half-life times with increased temperatures, pressures, and Eh. Since, most of these compounds are not normally biodegradable, hydrolysis is expected to be the main mechanism of transformation.

Half-life times can be estimated fairly accurately if rate constants are known for the compound at the appropriate temperature, pH, ionic strength, etc. However, the amount of data available is limited, and even though extrapolations can be made from one temperature to another, such extrapolations often introduce large errors.

Microbiological Degradation

Biodegradation can result from a variety of processes.[60-62] These processes include mineralization, detoxification, cometabolism, activation, and defusing. Mineralization is the conversion of organic wastes to inorganic wastes. Detoxification is the conversion of toxic compounds to nontoxic compounds. Cometabolism is the conversion of one organic compound to another without the microorganism using this process as a nutrient. Activation is the conversion of a nontoxic compound to a toxic compound. Defusing is the process of converting a compound potentially capable of becoming hazardous to another non-hazardous compound by circumventing the hazardous intermediate. Although defusing has been confirmed in the laboratory, it has not been identified in the environment.

The first question with respect to biodegradation most certainly is: When do any microbes exist in the injection zone, or can microbes capable of converting organic wastes to non-hazardous wastes exist at those conditions? Several researchers have attempted to answer this question.

DiTommaso and Elkan[63] analyzed a saline aquifer at the depths of 850 to 1000 ft. Much of the waste injected into this zone contained organic compounds such as acetic acid, formic acid, and methanol. About 3000 organisms/ml were isolated from the unpolluted aquifer. Most of the organisms identified were aerobes typically found in aquatic environments. The most common genera include Agrobacterium, Pseudomonas, Proteus, Bacillus, Aerobacter, Coryne bactor, Arthobacter, and Micrococcus. Conversely, samples taken after waste injection were found to contain primarily anaerobic methanogenic bacteria.

Christofi et al.[64] investigated several underground mines in Europe for the presence of microbiological activity. The depth of mines from which

samples were taken varied from 600 to more than 3000 ft below the ground surface. Microorganisms were found in all wells, although the greatest variety was found in the least saline aquifer. Salinity varied from less than 5.7×10^2 mg/l chloride to greater than 1.32×10^5 mg/l chloride. The original report should be consulted for more details.

Grula and Grula[65] discussed the degradation of wastes in subsurface type conditions. They noted that aerobic degradation usually is more efficient than anaerobic degradation, that some compounds such as aromatic chemicals can be degraded only by aerobes, and that higher temperatures are not as limiting for aerobes as for anaerobes. Grula and Grula[65] studied various compounds to determine which microorganisms and which supplemental nutrients would be necessary.

Additional research has shown that once the injection of hazardous wastes begins, other microorganisms that can utilize the wastes often appear and remain in the reservoir while the wastes are being injected. Grula and Grula[65] evaluated a number of organic compounds including nitriles, carboxylic acids, alcohols, amines, benzoic acids, phenols, ketones, aldehydes, nitro-aromatic compounds, and others. These compounds were subjected to enriched cultures to determine which organisms would be capable of incorporating and modifying which compounds. The effect of temperature, pressure, and mixed culture systems was also studied.

Elkan and Horvath[66-67] showed that upon injection of organic wastes the injection wells became more anaerobic in nature. Unlike the biological system of the unpolluted aquifer, the microorganisms in the injection zone during the period of waste disposal was dominated by methanogenic and sulfate-reducing bacteria. Additional laboratory model studies supported this conclusion. Microbial populations increased by seven or more orders of magnitude when

waste was introduced into the model. The effects of pressure varied. Degradation rates of formic acid increased as pressure was increased to 500 psi, but the degradation rates decreased again when pressures were further increased to 4,000 psi.

Wilson et al.[68] showed that certain chlorinated alkanes and alkenes were not degraded in materials normally found in deep subsurface environments. Other compounds, such as toluene and styrene, were readily degradable under the same conditions, although not equally so in different environments. Thus, Wilson et al.[68] recommended that biodegradation should not be depended upon for waste degradation unless the particular waste has been tested in the materials encountered and at the likely downhole conditions.

Similarly, Rittman et al.[69] conducted studies of biodegradation for certain compounds. This study discussed the microorganism biofilm model that presumably is formed to degrade the waste chemicals near the point of injection. Correlation of results with model predictions supported the formation of a biofilm. Some individual compounds, such as naphthalene and heptaldehyde, were degraded, whereas others such as haloforms were not.

Horvath[70] provides a good review of some of the studies conducted on biodegradation of wastes in subsurface environments and summarizes some of the processes involved in the degradation of such compounds as acetate, formate, methanol, formaldehyde, and aromatic acids. Horvath[71] also developed a laboratory model to evaluate these processes. These studies indicated an interesting observation concerning methane and sulfate-reducing bacteria. Apparently, even though the required nutrients were available, methanogenic bacteria did not proliferate, whereas the sulfate-reducing bacteria did in the zone studied. This behavior may have occurred because of the pH that predominated for the test and supported work done by others who indicated that

the two types of bacteria are mutually exclusive. Obviously, the degradation of injected wastes will depend upon which type of bacteria prevails. Methane-producing and sulfate-reducing bacteria do not degrade the same compounds.

Healy and Daughton[71] provide a good literature review of biodegradation in the groundwater. The authors concluded that even though several studies have shown the existence of bacteria in the subsurface environment, other factors necessary for fate prediction remain undetermined. The true origin of these bacteria has not been established, the level of activity for these bacteria is not always known, and the importance of other nonbiological processes already discussed in microbial degradation are all important topics that need further study.

Finally, although it is not of direct importance, the effect of pressure on bacteria was studied by Zobell et al.[72-75] For example, as pressures were increased from 1 to 400 atmospheres, E. Coli growth and reproduction was retarded, and above 400 atmospheres, the death rate was accelerated.[70] A number of other bacteria were also tested in this range, although the results varied from one type to another.[73] In general all growth and reproduction processes decreased with increasing pressures to 600 atmospheres.[73] Bacteria isolated from the marine environment at depths normal to these same pressures grew well in the laboratory studies and particularly at the slightly warmer conditions.[73] The effects such pressures have on the metabolic rates are presently unknown.

In summary, microbial degradation often is a very important mechanism by which certain hazardous wastes may be transformed to non-hazardous wastes. Bacteria have been identified in the subsurface environment. Within certain reasonable limits, bacteria are capable of surviving relatively hostile environments. Studies have also shown that transformation processes via

biological pathways can be very complicated and difficult to establish. Therefore, this method should not be depended upon for waste detoxification in the subsurface environment, unless pilot studies have established the existence of these processes.

FIELD CASE STUDIES

Belle Glade, Florida

McKenzie[76] discussed a case study concerning the upward migration and geochemical interactions of an acidic industrial waste injected into a saline aquifer near Belle Glade, Florida. The hot acidic liquid waste generated at a furfural plant at Belle Glade was injected into the lower part of the aquifer between depths of 1485-1939 ft. The injection of the waste began in 1966. Within 27 months, effects of wastes were detected at a shallow monitoring well in the upper part of the aquifer.

The analysis of the water samples indicated that the wastes were transported upward and laterally. This migration was indicated by a decrease in the sulfate/chloride ratio and a corresponding increase in the hydrogen sulfide concentration in the observation well water.

Remedial actions were taken. The wastes were injected into a deeper portion of the injection zone (2200 ft). However, when the wastes continued to migrate upward into the shallow well, the wastes were injected even deeper (3000 ft). The effectiveness of this latest strategy is not known. McKenzie[76] concluded that the carbonate aquifer could not contain the hot acidic wastes. No extensive work was performed to determine the areal extent of the zone of contamination.

The first reaction involving the waste with the limestone formation was neutralization of the acids. As a result, the concentration of calcium,

magnesium, and silica increased in the waste solution. Sulfate-reducing bacteria present in the formation converted sulfates to sulfides. The presence of hydrogen sulfide produced by the bacteria and the subsequent decrease of sulfate/chloride ratio was one of the indicaters of fluid migration.

Wilmington, North Carolina

From May 1968 to December 1972, an industrial organic waste derived from the manufacture of dimethyl terephthalate was injected at a rate of about 300,000 gal/day into a sedimentary aquifer containing saline water at a site near Wilmington, North Carolina. The injection zone consisted of multiple zones ranging in depth from about 850 to 1,000 ft. The injection of waste was started in May 1968 and was stopped in December 1972. The injection was discontinued after the operators determined that disposal of this waste into the reservoir was not desirable. Even though injection of the waste was discontinued, monitoring of the waste movement and subsurface environment were continued into the mid-1970s. Peek et al.[77] reported the initial results at an international symposium on underground waste. A final report documenting the laboratory and field results of this project was presented by Leenheer et al.[78-79] The following paragraphs summarize this investigation.

A site study was initiated in June 1971 to investigate the waste aquifer interactions. The first stage of the study involved the characterization of the industrial waste, the native ground water found in the injection zone, and the site hydrogeologic conditions. Sodium chloride was found to be the major dissolved solid constituent of the native ground water. The average dissolved solid concentration was estimated to be about 20,800 mg/l. The average dissolved organic carbon of the industrial waste was determined to be about

7,100 mg/l and comprised acetic acid, formic acid, p-toluic acid, formaldehyde, methanol, terephthalic acid, phthalic aid, and benzoic acid. Before injection, the organic waste was neutralized to a pH of 4 by adding lime. Therefore, the major inorganic constituent of the waste was calcium (about 1,300 mg/l).

The second stage of the study determined the waste-aquifer interactions at various observation wells. Water samples were taken from three observation wells located 1,500 to 2,000 ft from injection wells. This second stage revealed the following observations.

- The waste organic acids were responsible for the dissolution of carbonate minerals, alumino-silicate minerals, and the sesquioxide coatings on the primary minerals in the injection zone.
- The waste organic acids dissolved and formed complexes with iron and manganese oxides. These dissolved complexes reprecipitated when the pH increased to 5.5 or 6.0, due to neutralization of the waste by the aquifer carbonates and oxides.
- The aquifer mineral constituents sorbed all waste organic compounds except formaldehyde. The sorption of all organic acids except the phthalic acid was increased with a decrease in waste pH.
- Phthalic acid was complexed with dissolved iron. The concentration of this complex decreased as the pH increased, because the complex coprecipitated with the iron oxide.
- Biochemical waste transformation occurred at low waste concentrations. This resulted in the production of methane. Additional microbial degradation of the waste resulted in the reduction of sulfates to sulfides, and the reduction of ferric ions to ferrous

ions. Additional biodegradation does occur slowly in this subsurface environment.

The wells became plugged after a few months of injection because of the reactive nature of the wastes. Thus, compatibility of wastes with fluids and minerals in the injection zone should be considered before injecting these types of wastes. The plugging resulted in this case from the precipitation of the initially dissolved minerals, from the formation of gaseous products such as carbon dioxide and methane, and from the dissolution of the bond between the cement grout surrounding the well casing and confining beds by the organic acids. As a result of the plugging in the formation, the waste leaked upward into the shallower zones.

Pensacola, Florida (American Cyanamid)

Vecchioli et al. [80-81] summarized the findings of an investigation on the fate of an industrial waste liquid containing organonitrile compounds and nitrate. These wastes were injected into the lower limestone formation of an aquifer near Pensacola, Florida.

Chemical analyses of water from a monitor well and the backflow from the injection well indicated that organic compounds were converted to carbon dioxide and the nitrate was reduced to elemental nitrogen. These microbiological transformations were virtually complete within a short distance from the injection well.

Sodium thiocyanate contained in the waste remained unaltered during the movement through the injection zone. Thus, sodium thiocyanate was used to detect the degree of mixing of waste liquid with native water at an observation well. Analysis of samples taken from the observation well indicated

that the waste liquid was completely free of organonitriles and nitrate. An 80 percent reduction in chemical oxygen demand was also observed.

Pensacola, Florida (Monsanto)

Pascale et al.[82] discussed the hydraulic and chemical data collected at a deep-well, waste-injection system near Pensacola, Florida. The industrial liquid wastes generated at a Monsanto Company chemical plant consisted of nitric acid, inorganic salts, and numerous organic compounds. The wastes were injected into a saline water-filled limestone aquifer.

The report summarized the data collected between 1970-1977. These data include injection rates, injection volumes, injection pressures, water levels, and laboratory analyses of water samples taken from three monitor wells.

The wellhead pressure averaged 180 psi in March 1977, and the hydraulic pressure gradient was 0.53 psi/ft of depth at the top of the injection zone. While the chemical character of the water collected from the shallower observation well remained unchanged, the water samples from the deeper monitor well to the south showed an increase in concentrations of bicarbonate, dissolved organic carbon, and gas content. These observations indicated that microbial degradation of the wastes was occurring in the injection zone.

CONCLUSIONS

Many conclusions were presented by the papers reviewed in this report; some of the more significant ones are as follows:

- The basic compatability test conducted by mixing waste fluids and reservoir fluids does not always give meaningful results. The test must be conducted under reservoir conditions. Precipitates, if formed in the compatibility test, may or may not plug the well depending upon the type of precipitate formed.

- For non-organic wastes, solution pH is critical for determining the ultimate fate. The identity of soluble species, solubility products, adsorption characteristics, and chemical interactions are some of the variables affected by pH.
- The brine concentration, even though not listed as hazardous, is important in affecting clay stability and adsorption characteristics.
- The presence of organic complexing agents may or may not affect the mobility of heavy metals in the reservoir.
- Adsorption of non-organic wastes is dependent upon a number of factors, such as Eh, pH, clay type, and the presence or absence of iron oxides and hydroxides.
- Mathematical models do successfully predict certain reaction processes. However, some interactions have not been modeled yet.
- Pentachlorophenols adsorb onto clays by a combination of ion exchange and Van der Waals forces.
- The major mechanism of degradation for certain halogenated hydrocarbons is hydrolysis.
- Microbial degradation of organic hazardous wastes has been shown to be useful in decontamination after deep-well injection. Wastes can support growth of certain bacteria during the injection process. However, results are not always predictable, and studies suggest that each case should be evaluated individually to determine the feasibility of the process.
- Some case studies corroborate the interrelationships of degradation processes discussed in this report.

RECOMMENDATIONS

The authors of this report recognize that all areas discussed need to be investigated further. Additional research in all areas will provide the foundation needed for predicting the ultimate fate of hazardous wastes disposed of by deep-well injection. However, the following areas are considered more productive in the near-term and are recommended for Phase II and Phase III of this project.

Phase II

Conduct dynamic coreflood studies of selected phenols to determine their short-term fate (30 to 60 days) under typical reservoir conditions created in the laboratory. Such parameters as solution pH, salt concentrations, temperatures, clays, and waste concentration should be evaluated with respect to precipitation, adsorption, permeability reduction, and thermal degradation.

Phase III

Conduct dynamic coreflood and/or related studies of selected hazardous wastes to determine their fate in subsurface environments. Although the exact scope has not been agreed upon, the following suggestions are possible. Expand the work conducted in Phase II by doing similar experiments on other cores or with other organic waste compounds. Investigate interactions of the phenols tested in Phase II with confining layer materials (this investigation probably should be done using hydrothermal reactors rather than corefloods). Extend the work in Phase II to include the effects of microorganisms on the degradation of phenols.

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